Catalytic Activity of Silver and Gold Metals Doped with Alkali Metals

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When alkali metals are brought into contact with silver or gold, catalytic activity for hydrogen activation reactions results which is higher than that for each of the constituent metals. The order of the activity per mole of alkali metal for the H_2-D_2 exchange reaction is Ag–Cs>Ag–K>Au–Cs>Ag–Na. The Ag–Cs and Ag–K systems absorb considerable amounts of hydrogen. The nature of the active sites and the contact effect of the IB metal with the alkali metal are discussed.

It has been reported that the addition of alkali metals to various materials results in marked changes in their catalytic properties.[1-3] The compounds formed between alkali metals and various aromatic compounds or graphite are of special interest because they exhibit marked catalytic activity for the activation of hydrogen molecules, although individually both constituents are of low activity in activating hydrogen molecules. Ichikawa *et al.* reported in a preliminary communication[4] that considerable catalytic activity was created when alkali metals were brought into contact with silver film, while the effect was not so large in the case of gold film. Since both silver and gold are regarded as inactive with respect to hydrogen activation, the study of the effect of the addition of alkali metals on the catalytic activity and selectivity may give clues to understanding the nature of catalysis for hydrogen activation. In this study the activation of molecular hydrogen on silver- and gold–alkali metal catalysts, as well as on each of the constituent elements, was examined in detail.

Experimental

Preparation of Catalysts. *Ag–Alkali Metal*: Silver powder was obtained by reducing silver oxide (Wako Pure Chemical Industries, 99.0%) with hydrogen at *ca.* 100 °C. Sodium (Merck) and potassium (Wako) metals were purified by repeated distillation under vacuum. Cesium metal was prepared *in vacuo* by a reaction between cesium chloride and calcium metal at 600 °C[5] and purified by repeated distillation. The alkali metals thus obtained were evaporated onto the silver powder in an evacuated glass vessel, and the resulting catalysts were subjected to heat treatments at various temperatures between 100 and 200 °C under vacuum. The surface areas of the catalysts were 0.1—0.5 m^2/g, which were determined by the BET method. The composition of the catalysts was determined by titration of the alkali metals. The sodium-doped silver catalyst (Ag–Na) weighed 9.39 g, which consisted of 9.38 g of Ag and 0.01 g of Na (0.10 wt%, 5×10^{-4} mol), (Ag–K) 9.8 g (Ag 9.1 g, K 0.7 g (7 wt%, 2×10^{-2} mol)) and (Ag–Cs) 9.5 g (Ag 8.7 g, Cs 0.8 g (8.3 wt%, 6×10^{-3} mol)).

Au–Cs: Gold powder was obtained by reducing chloroauric acid (Wako) with hydroquinone.[6] Cesium was introduced onto the gold powder sealed in a Pyrex glass tube, as shown in Fig. 1, by the "dual furnace" method[7] under vacuum. The gold powder was charged in A of the figure, and the cesium metal in B. A and B were heated

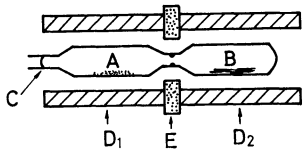

Fig. 1. Schematic diagram of "Dual Furnace" method. A: IB metal, B: alkali metal, C: breakable seal, D_1, D_2: furnaces; each furnace can be operated independently. E: insulating ring.

for 35 days at 146 and 140 °C, respectively. The catalyst weighed 1.1 g (Au 0.9 g, Cs 0.2 g (19 wt%, 2×10^{-3} mol)) and was dark-blue-violet.

Alkali Metals: The alkali metals, purified as above, were evaporated *in vacuo* onto the inside wall of a Pyrex glass tube which had been baked out beforehand at temperatures between 200 and 300 °C. The sodium film (Na) weighed 1.2×10^{-4} g, the potassium film 1 g, and the cesium film 1.2 g and the total geometrical surface areas were 50—90 cm^2.

Reactants. Commercial reactant gases were purified as follows. Hydrogen was passed through a DEOXO catalyst (Engelhard Industries, Ltd.) at room temperature and then through a 5A molecular-sieve column cooled to 77 K. Deuterium was passed through a 5A molecular-sieve column and then an activated charcoal column at 77 K. Ethylene was frozen at 77 K, evacuated, and then was passed through a dry ice–methanol trap. Propylene was purified by repeated freeze, evacuation and thaw cycles.

Apparatus and Procedures. The apparatus employed for the reactions was a closed circulating system whose dead volume was about 300 cm^3. The total pressures of the reactant gases were ordinarily between 13 and 27 kPa. The pressure change during the course of the reaction was followed using a mercury manometer. The reacting gas mixtures were analyzed by gas chromatography,[8] infrared spectroscopy, mass spectrometry, and microwave spectroscopy. The activity of the catalysts remained unchanged upon repeated runs and each run was normally carried out without pretreatment.

Results

Absorption of Hydrogen and the H_2-D_2 Exchange Reaction. When hydrogen was introduced into various catalyst systems, the absorption of hydrogen took place at various extents, as given in Table 1. The absorption of hydrogen by Ag–Cs, for example, is shown in Fig. 2. A negligible amount of thermal desorption of the

Table 1. Catalytic activity of the catalysts

Catalyst	Alkali metals			IB metal	Binary system 1[a]		Binary system 2[a]	
	Na	K	Cs	Ag	Ag–K	Ag–Cs	Ag–Na	Au–Cs
H_2 absorption[b] /cm³ STP (t/°C)					3×10^3 (46)	3×10^4 (23)	≈0 (120)	≈0 (22)
Ea/kJ mol^{-1} [c] (t/°C)	109±8 (150—250)	49±4 (35—120)	34±4 (25—100)	46±8 (90—220)	32.8±0.4 (−65—50)	26±1 (T[d]—55)	76±8 (50—100)	50±4 (110—140)
						<10.1 (−80—T[d])		15.5±0.4 (0—110)
k_1[e]/h^{-1} g^{-1} (0°C)	$<2\times10^{-5}$	2×10^{-4}	3×10^{-2}	3×10^{-6}	1.5	1.7	1×10^{-4}	1×10^{-1}
k_1[f]/h^{-1} (0°C)	$<5\times10^{-4}$	8×10^{-3}	4	—	8×10^2	3×10^3	2	7×10
$\log(A^g$/h^{-1} g$^{-1})$	<14±1	5.7±0.3	5.1±0.4	3.7±0.5	6.3±0.1	4.2±0.3	10.5±1.0	4.8±0.2
$\log(A^h$/h$^{-1})$	<15±1	7.3±0.3	7.2±0.4	—	9.0±0.1	7.4±0.3	14±1	7.6±0.2
k_1[i]/h^{-1} g^{-1} (t/°C)	—	—	1×10^{-1} (100)	—	1×10^{-2} (94)	4×10^{-1} (100)	—	2×10^{-2} (140)
Site					A[j] and B[k]		A	

a) Binary system 2 forms metallic compounds, whereas binary system 1 does not. b) The amount of saturated absorption of hydrogen per mole of alkali metal in the catalyst. c) Apparent activation energy for the H_2-D_2 exchange reaction. d) $-40\,°C<T<-23\,°C$. e) Rate constant for the H_2-D_2 exchange reaction per gram of the catalyst. f) Rate constant for the H_2-D_2 exchange reaction per mole of alkali metal in the catalyst. g) Frequency factors for the H_2-D_2 exchange reaction per gram of the catalyst. h) Frequency factors for the H_2-D_2 exchange reaction per mole of alkali metal in the catalyst. i) Rate constants for ethylene hydrogenation. j), k) See text.

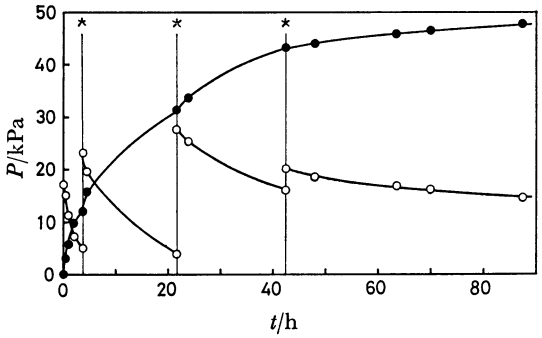

Fig. 2. Absorption of hydrogen on Ag–Cs at 23 °C. ○: pressure of hydrogen gas, ●: total decrease in pressure, *i.e.*, amount of absorbed hydrogen (The pressure decrease of 1 kPa corresponds to the absorption of 0.35 cm³ STP/g-catalyst.). At the point denoted by * hydrogen was added into gas phase.

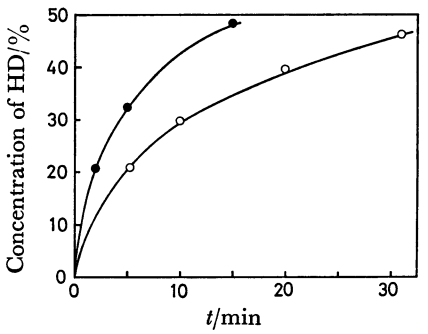

Fig. 3. The H_2-D_2 exchange reaction over Ag–Cs. The total pressure of reacting gas was 8 kPa. The equimolar mixture of H_2 and D_2 was introduced over the catalyst with preabsorbed hydrogen of 170 cm³ STP per 9.5 g catalyst. Reaction temperature; ○: 0 °C, ●: 23 °C.

absorbed hydrogen took place *in vacuo* below 170 °C, the amounts of saturated absorption remaining unchanged. No appreciable hydrogen absorption was detected on the alkali metals in the absence of silver under the same conditions. At higher temperatures, however, alkali metals reacted with hydrogen, forming hydrides.

When an equimolar mixture of H_2 and D_2 was introduced over Ag–K and Ag–Cs systems, the H_2-D_2 exchange reaction took place at a rather high rate at room temperature, as shown in Fig. 3. When deuterium was introduced over the Ag–K and Ag–Cs catalysts, which contained preabsorbed hydrogen, at a temperature above 100 °C and at room temperature, respectively, at first HD quickly appeared in the gas phase but soon slowed down, as shown in Fig. 4. The rate of HD formation after the initial surge was 10^2 or 10^3 times slower than that in the H_2-D_2 exchange reaction under similar reaction conditions. The deuterium preabsorbed over Ag–Cs participated in the hydrogenation of ethylene and propylene at 100 °C, whereas the deuterium in the alkali metal hydrides, in the absence of silver, did not.

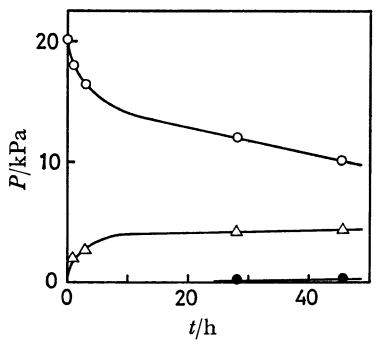

Fig. 4. The exchange reaction between gaseous deuterium and the absorbed hydrogen on Ag–Cs at 23 °C. The total amount of hydrogen preabsorbed at 23 °C was 150 cm³ STP per 9.5 g catalyst. ○: D_2, ●: H_2, △: HD.

The H_2-D_2 exchange reaction was of first order with respect to the total pressure. The dependence of the reaction rate with pressure for Ag–K at 0 °C is shown

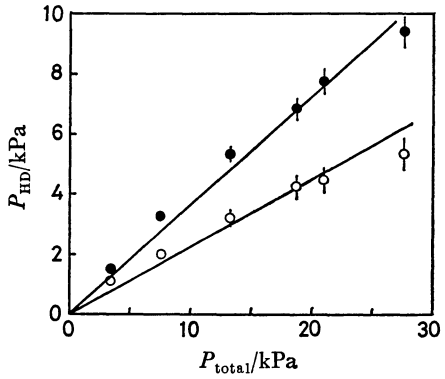

Fig. 5. Pressure dependence of the rate of the H_2-D_2 exchange reaction over Ag–K at 0 °C, with the initial amount of H_2 equal to that of D_2. Reaction time; ○: 2 min, ●: 6 min.

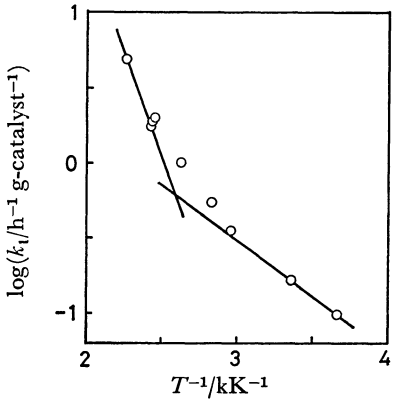

Fig. 6. Temperature dependence of the rate constants of the H_2-D_2 exchange reaction over Au–Cs.

in Fig. 5. The rate constant k_1 was calculated using the equation,

$$k_1 = -\frac{1}{t} \ln \frac{[HD_\infty]-[HD_t]}{[HD_\infty]},$$

where $[HD_t]$ and $[HD_\infty]$ are the concentrations of HD at time t and that at equilibrium, respectively. The temperature dependence of k_1 over Au–Cs is shown in Fig. 6. The apparent activation energies for the reaction over various catalysts are listed in Table 1. The activation energies were not affected by the heat treatments, although the rate of the exchange reaction was changed. The catalytic activity of each of the Ag–alkali metal catalysts was increased by repeated heat treatments and approached a saturated value at a given temperature between 100 and 200 °C under vacuum. The activity decreased, however, when the temperature of the heat treatment was higher than 200 °C. In the case of Au–Cs, the catalytic activity remained constant for heat treatments up to a temperature of 260 °C *in vacuo*. In the case of Ag–K and Ag–Cs catalysts, the rate of the H_2-D_2 exchange reaction was neither affected by the preabsorbed hydrogen nor by the presence of ethylene. The activity of Au–Cs was markedly enhanced (more than ten times) when fresh cesium metal was additionally evaporated onto the catalyst, but decreased and finally reached the original value after repeated heat treatments. The first order rate constants for the exchange reaction on each catalyst are listed in Table 1. In some systems, the measurements were carried out at temperatures above 0 °C, and the values of the rate constant k_1 at 0 °C were then estimated from their temperature dependences. The results given in Table 1 lead to the following conclusions.

(1) The catalytic activity of silver for the H_2-D_2 exchange reaction is increased by contact with alkali metals as follows:
3×10 for Ag–Na/Ag, 5×10^5 for Ag–K/Ag, and 6×10^5 for Ag–Cs/Ag.

(2) The increase in the activity per mole of the alkali metals by contact with IB metals are as follows: 5×10^3 for Ag–Na/Na, 1×10^5 for Ag–K/K, 7×10^2 for Ag–Cs/Cs and 2×10 for Au–Cs/Cs.

(3) The activity per mole of the alkali metal was in the following increasing orders:
Na<K<Cs and Ag–Na<Au–Cs<Ag–K<Ag–Cs.

The frequency factors for the exchange reaction are listed in Table 1.

Hydrogenation of Ethylene and Propylene. When ethylene or propylene was brought into contact with Ag–Cs which contained preabsorbed hydrogen (or deuterium) at 100 °C, olefin adsorption took place and simultaneously ethane or propane (with deuterium) appeared in the gas phase. Cs metal adsorbed the olefins at 100 °C and the alkanes were formed concurrently through self-hydrogenation of the olefins. When hydrogen was introduced after ethylene had been preadsorbed on Ag–Cs and Cs, 10—20% of the preadsorbed ethylene reacted to form ethane with a small amount of 2-butenes. On the other hand, most of the propylene adsorbed on Ag–Cs was desorbed into the gas phase upon the introduction of hydrogen with only a small amount of propane, followed by slow hydrogenation. Ag–K containing preabsorbed hydrogen adsorbed little ethylene at 20—50 °C, as hydrogen is adsorbed more strongly than ethylene.

The hydrogenation of ethylene with molecular hydrogen to form ethane took place on Ag–Cs, Ag–K, Au–Cs, and Cs, and the pressure dependence of this process was first order with respect to the amount of ethylene and zeroth order with respect to the amount of hydrogen, as shown in Fig. 7. The reaction rate can accordingly be expressed by the equation,

$$\text{rate} = k_1'[C_2H_4],$$

where k_1' is the rate constant and $[C_2H_4]$ is the partial pressure of ethylene. The k_1' for each catalyst is given in Table 1.

The initial rate of ethylene hydrogenation over Ag–Cs between hydrogen gas and ethylene was more than fifty times as fast as that between ethylene and preabsorbed hydrogen in the absence of gaseous hydrogen at 100 °C.

It was also demonstrated that hydrogen in the gas phase at higher pressures inhibits the production of propane over Ag–Cs and Cs at 100 °C, as is shown in Fig. 8.

The hydrogen exchange reaction between propylene and deuterium was approximately 100 times faster than the hydrogenation of propylene on Au–Cs at 215 °C. The isotopic distribution of the deuterated propylenes

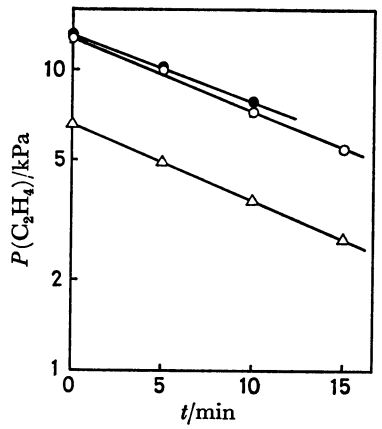

Fig. 7. The hydrogenation of ethylene in the presence of gaseous hydrogen over Ag–Cs with preabsorbed hydrogen at 0 °C. Total amount of the preabsorbed hydrogen was 170 cm³ STP per 9.5 g catalyst. The initial composition of the gaseous mixture; ○: C_2H_4 12.9 kPa, H_2 14.0 kPa, △: C_2H_4 6.6 kPa, H_2 13.4 kPa, ●: C_2H_4 13.2 kPa, H_2 6.6 kPa.

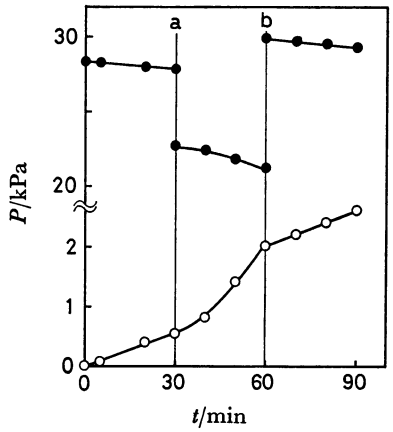

Fig. 8. The hydrogenation of propylene over Ag–Cs with preabsorbed hydrogen at 104 °C. The total amount of absorbed hydrogen was 170 cm³ STP per 9.5 g catalyst. The initial gas was composed of 15.0 kPa of propylene and 13.3 kPa of hydrogen. a) Hydrogen gas was partially removed. b) Hydrogen gas was added. ●: Total pressure of gas phase. ○: Propane pressure. Hydrogen absorption was saturated and the partial pressure of C_3 species in the gas phase was not changed in the course of reaction, and, consequently, the decrease in pressure during the reaction corresponds to the production of propane.

determined by their microwave spectra[9] indicated that no hydrogen exchange takes place at the 2-carbon positions and only the hydrogen at both end carbons participates in the exchange.

Discussion

It is, thus, demonstrated that alkali metal-doped IB metal catalysts have higher catalytic activities for hydrogen activation reactions per mole of each constituent than each of the IB metals or alkali metals, as given in Table 1. The activation energies for the H_2-D_2 exchange reaction were also changed by the doping. This behavior is similar to that of other alkali metal-doped catalysts, such as potassium-condensed aromatic hydrocarbons.[2] Thus, when they are brought into contact, the electron donor (alkali metals) and acceptor (IB metals) exhibit new catalytic activity, higher than each of the constituents.

The H_2-D_2 exchange reaction was of first order with respect to the total pressure, and the hydrogenation of ethylene was of first order with respect to the amount of ethylene and of zeroth order with respect to that of hydrogen. In addition to the kinetic expression, the H_2-D_2 exchange reaction was not retarded by the presence of ethylene, which strongly suggests that hydrogen is more strongly adsorbed than olefins.

It has been reported that the Ag–Na and the Au–alkali metal systems form metallic compounds, whereas no such compounds are formed in the Ag–K and Ag–Cs systems.[10] The latter group is more active in activating molecular hydrogen. The activity of these doped catalysts also depends upon the electropositivity of the alkali metals, which is in the following increasing order, Na<K<Cs. A higher electropositivity generally results in a higher catalytic activity.

The behavior of the IB metal–alkali metal catalysts suggests the following scheme for the active sites relevant to hydrogen activation. The IB metal–alkali metal catalysts appear to possess at least two kinds of active sites for hydrogen activation and absorption, site (A) and site (B). The H_2-D_2 exchange reaction proceeds mainly *via* adsorbed hydrogen (or deuterium) on site (A), while the absorption of hydrogen takes place on site (B), most of the hydrogen thus absorbed hardly participating in the exchange.

Site (A) is apparently much more active when no metallic compounds are formed between the constituents or if the alkali metals are more electropositive. The heat treatment under vacuum changes only the number of sites, the apparent activation energy remaining unchanged. Site (A) may be considered to be located at the doped alkali metal which is in contact with the IB metal because of the similarity in the reaction kinetics over site (A) with those over alkali metals; *i.e.*, the similarity of the pressure dependences in the H_2-D_2 exchange reaction and in ethylene hydrogenation. The contact with IB metals reduces the activation energies for the reaction on the alkali metal.

In the case of Au–Cs, further addition of cesium by evaporation produced higher activity, but subsequent heat treatments reduced the enhanced activity to its original magnitude. Two different activation energies for the H_2-D_2 exchange reaction were observed over the reaction-temperature range, as shown in Fig. 6.

Hydrogen is strongly absorbed on site (B) such that the absorbed hydrogen is not desorbed by mild heat treatments *in vacuo*. Site (B) is less active than site (A) for the H_2-D_2 exchange reaction and the hydrogenation of ethylene. In the case of hydrogenation of propylene, higher hydrogen pressures even retard the rate of hydrogenation, as shown in Fig. 8.

Since the atomic ratio of the total amount of absorbed hydrogen to cesium was more than two on Ag–Cs, as

given in Table 1, the formation of alkali metal hydride cannot account for all of the absorbed hydrogen, while silver metal alone absorbs no hydrogen. It is thus revealed that the contact of cesium with silver exhibits new activity not only for hydrogen activation reactions, such as the H_2-D_2 exchange and hydrogenation reactions, but also for hydrogen uptake. Although the reason why such new activity appears is a matter of conjecture, electron donation from the alkali metal to the IB metal is most probably associated with this phenomenon.

Conclusion

High catalytic activity for hydrogen activation reactions was produced by the contact of alkali metals with IB metals. The addition of alkali metals activates the silver surface for the chemisorption of hydrogen. The enhanced activity of alkali metals upon contact with IB metals is due to the decrease in the activation energy.

The new catalytic activity is considered to be caused by electron donation from the alkali metal to the IB metal and not by the formation of metallic compounds.

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